Use of X-ray fluorescence spectroscopy for the determination of rare-earths contained in the concentrates and in landfills from the beneficiation plant of Gakara rare-earth deposit in Burundi

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Abstract

The Gakara rare-earth ore deposit in Burundi is the only operating rare-earth mine in Africa and one of the richest rare-earth deposits in the world with an in-situ content of 47 to 67% rare-earth oxides (REO). However, although the country has significant mineral resources, Burundi has not yet developed a mining industry and even the Kabezi rare-earth concentration plant only produces concentrates, exported as such to the raw state, without any added value. Prior to the results of the present study, no quantitative data from researchers was available on the content of the said concentrate, much less on the nature of the substances that contain it. Therefore, the present research work focused on quantitative analysis by X-ray fluorescence spectroscopy on rare-earth concentrates and on landfills scattered around the said beneficiation plant. The findings of the present research work reveal that the rare-earth concentrate from Gakara rare-earth ore deposit in Burundi contains seven metals of this strategic ore including lanthanum (20.5% in elements; 18.0% in oxides), yttrium (0.16%; 0.15%), cerium (37.75%; 33.75%), praseodymium (2.80%; 2.63%), neodymium (12.14%; 10.00%), samarium (1.00%; 0.90%) and gadolinium (0.47%; 0.35%). With a total rare-earth elements (TREE) content of 74.84 ± 0.33%, the Gakara rare-earth concentrate can be refined into seven rare-earth metals. The corresponding total rare-earth oxide (TREO) content is of 65.78 ± 0.29%. Such findings are highly revealing and constitute a critical step which must lead to an in-depth research on the optimization of a technological separation and purification process which could be used specifically for this deposit considered as one of the most strategic globally. Regarding the waste dumps, the present research found that they contain quantities of thorium (0.127%) and lead (0.237%) at levels that should not be ignored. No uranium was detected.

Keywords: XRF; *Rare-Earth; X-Ray Fluorescence; Monazite and Bastnaesite Concentrate; Gakara Project in Burundi; S*imulated Moving Bed.

1. Introduction

Rare-earth elements (REE), also called rare-earth metals or simply rare-earths, are the seventeen elements that are found grouped together in the ore because of their chemical and physical similarities and include the 15 elements of the periodic table of the elements, commonly called lanthanides. To these 15 lanthanides are also added scandium and yttrium which have chemical properties similar to the fifteen lanthanides. Therefore, the chemical elements that bear the name of "rare-earth" are seventeen in number (Long *et al.*, 2010). REEs are informally subdivided into light rare-earth (LREE - La to Sm) and heavy rare-earth (HREE - Eu to Lu and Y) (Kato et al., 2011). Ore deposits containing predominantly yttrium and HREEs include gadolinite, xenotime, samarskite, euxenite, fergusonite, yttrotantalite, yttrotungstite, yttrialite. Minerals containing predominantly LREEs include bastnaesite, monazite, allanite, loparite, ancylite, parasite, lanthanite, chevinite, cerite, stillwellite, britholite, fluocerite and cerianite. However, commercially operating mines around the world mainly extract bastnasite, monazite and xenotime ores. Bastnaesites are fluorocarbons with the formula $(Ce, La)CO_3F$ or $(Y, Ce)CO_3F$. Monazite has the general formula $(Ce, La, Nd, Sm, Gd, Y, Th)PO_4$ which can be divided into its variants, namely Monazite-Ce $(Ce, La Nd)PO_4$, Monazite-La $(La, Ce, Nd)PO_4$, Monazite-Nd $(Nd, La, Ce)PO_4$ and Monazite-Sm $(Sm, Gd, Ce)PO_4$.

REEs are important for high-technology and clean-energy applications (Humphries, 2013; Humphries, 2010; Long *et al.*, 2010; British Geological Survey, 2011; Kato *et al.*, 2011). They are critical components of many high-valued products such as petroleum refining catalysts, phosphors in color televisions and flat panel displays, permanent magnets, polishing powders, metal alloys, ceramics and rechargeable batteries for hybrid and electric vehicles. Approximately 60% of rare-earth metals are used in the formulation and manufacturing of magnets that are necessary for almost everyone's daily lives. Most of these magnets are key parts used in green technologies (electric and hybrid vehicles, wind turbines and energy storage), electronics, imaging systems and strategic defense systems including military aircraft. The primary defense application of rare-earth materials is their use in four types of permanent magnet materials commercially available, namely the Alnico magnets, Ferrites, Samarium-Cobalt, and Neodymium Iron Boron magnets (NdFeB). Neodymium magnets, the product derived from neodymium iron, boron, and samarium-cobalt, are considered as the world's strongest permanent magnets and are essential in the development of many military weapons on which they entirely depend. As numerical illustrations, a fighter jet needs 417 kg of rare-earth, a hybrid car more than 27 kg, a satellite 23 kg, a destroyer 2360 kg, and a submarine not less than 4170 kg of rare-earth (Grasso, 2013). Other NdFeB permanent magnets (30% w/w) (Mancheri *et al,* 2019) are widely used in hard drive disks, wind turbine generators, and electric vehicle motors. Three key REEs in NdFeB magnets are Nd, Dy, and Pr. The first two are among classified as critical materials by the U.S. Department of Energy, which aims at generating 20% of the electricity from wind energy by 2030 (Imholte *et al.,* 2018). Each direct-drive permanent generator for 1 MW of electricity will require between 160 to 650 kg of permanent magnets made from Nd, Pr, and Dy (Imholte *et al.,* 2018). Rare earth permanent magnets are also used in the motors of the hybrid and electric vehicles. It is estimated that each hybrid or electric vehicle requires 1.5 to 2.5 kg of REE-based permanent magnets (Elwert *et al.,* 2016). Other REEs are considered essential in the development of future technologies. This is particularly the case of lanthanum (La), which is already known for its use in the manufacture of rechargeable batteries, essential in the technology of electric vehicles, but also used to manufacture night vision goggles used during night military operations. In addition, current researches use La as dopant for a type of perovskites used as lithium solid ion electrolyte materials (Stramare *et al.*, 2003 ; Inoue *et al.*, 2006 ; Yizhou *et al.*, 2015) commonly called lithium lanthanum titanate oxides (LLTO), which are considered to be the best candidates for the formulation of all-solid-state batteries, the next generation of batteries that will be used in high-tech microelectromechanical systems (MEMS) (De Cliff *et al.*, 2012 ; De Cliff, 2022).

The global REE market is estimated at $4 billion annually and is growing at about 8% per year. The supply chain and demand of rare-earth have grown rapidly over the past 20 years, but their production has been limited to a few countries (Mineral Commodity Summaries 2020; U.S. Geological Survey). Currently, more than 95% of the world's rare-earth are produced in China from two types of ore deposits (Humphries, 2013; Humphries, 2010; Long *et al.*, 2010). The Bayan Obo deposit, considered to be the largest deposit rare-earth in the world, is an igneous carbonatite deposit dominated at 80% by LREE (U.S. Geological Survey, 2011; Kynicky *et al.*, 2012; Verplanck *et al*., 2014). The second, although small and low-grade, is a clay deposit (ion-adsorption clay) in southern China, which supplies all the heavy REEs demand globally (Long *et al.*, 2010; Kynicky *et al.*, 2012). The production chain of REEs or rare-earth oxides (REO) is long, complex and must be adapted to the particularities of each source of feedstock. There are essentially two sources feedstocks, namely rare-earth minerals ores deposits and recycling wastes materials containing rare-earths. In the case of ore deposits, the production generally begins with the beneficiation or concentration of the ore, and this leads to the production of the rare-earth concentrate. The concentrate is then processed to extract rare-earths into separated rare-earth oxides, which are refined into purified rare-earth metals (Figure 1).
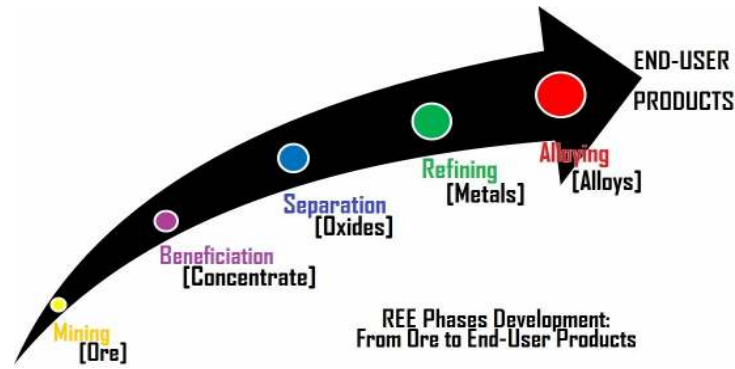
Figure 1: Different phases of development from a rare-earth ore to rare-earth alloys used in finished products such as magnets, to a range of end-user devices (from a simple smartphone to a nuclear submarine).

A review of current progress of rare-earth processing methods and technologies, focusing on extractant categories, has been recently published and includes liquid-liquid separation, solid-liquid extraction, column chromatographic separation, and solid extraction and separation methods (Traoré et al., 2023). In addition to this environmental aspect, REE production is also limited by the lack of technical expertise, due to the often too high investment cost in the development of alternative processes (Jordens et al., 2021). All this has resulted in China becoming the sole default buyer of all rare earth concentrates produced in the world, making other countries totally dependent on its stocks. This fact is best illustrated by the fact that even the bastnaesite concentrate from the Mountain Pass rare earth mine in California is shipped to China for further processing, meaning that the United States' supply of REE is entirely dependent on imports from abroad, almost exclusively from China. (Mineral, 2021). Taking advantage of this de facto monopoly, China has also halved its export quota since 2010. All this makes the development of new efficient and profitable processes for the production and valorization of REEs domestically by the producers themselves, highly desirable. Recently, a new and innovative technology using a two-zone ligand-assisted displacement (LAD) chromatography system was developed and patented in United States by the laboratory of Nien-Hwa Linda Wang, at Purdue University (Ding *et al.*, 2020). The Wang method uses a novel zoning approach that produces high purity (>99%) metals in high yields (>99%). This advanced new technology further has the potential to provide 100-times higher efficiency than liquid-liquid extraction methods and environmentally friendly purification of rare-earth metals from all recycled product sources, such as magnetic waste and ore-based sources, and helps transform the current linear REE economy to a circular and sustainable REE economy (processing of rare-earths ores to pure REEs, to products, to landfills; and again processing landfills to pure REEs, to products).

Of all the dozen rare-earth projects reported in Africa (Figure 2), as mapped by Harmer *et al.* (2016), one important of them is Gakara rare-earth project in Burundi, which actually produces a concentrate.

The Gakara rare-earth deposit is located about ten kilometers from the economic capital Bujumbura. This deposit has feature particularities as being the first and the only rare-earth mine in operation in Africa. It is also considered to be one of the richest rare-earth deposits in the world with an in-situ content of 47 to 67% rare-earth oxides (REO) [NS Energy, Gakara Rare-Earth Project]. Previous studies on the mineralogy of the Gakara rare-earths deposit have determined that the said deposit is a mixture of bastnaesites and monazites (Harmer *et al.*, 2016; Ntiharirizwa *et al.*, 2018). It has been suggested that initial REE mineralization of the Gakara ore consisted of coarse-grained bastnaesite which was subsequently brecciated, allowing the penetration of phosphate fluids which metasomatically transformed the bastnaesite into microcrystalline monazite. A range of mineralization types have been generated in response to the intensity of metasomatism, from pure and massive bastnaesite (massive mineralization), through mixed bastnaesite-monazite, to monazite-dominated (Breccia) mineralization (Harmer *et al.*, 2016).

However, according to annual reports of US Geological Survey (Cordier, 2020), the rare-earth oxide reserves of the Gakara rare-earth ore deposit (Figure 3) are not known. However, in December 2017 and according to JORC standards, the first resource estimate was of 1.2 million tons of ores spread over the Gasagwe, Murambi South and Gomvyi Center sites. These sites are said to contain 12,000 tons of high-grade ore resources, with an average in-situ grade of 55% TREO (total rare-earth oxide), while the Kiyenzi deposit is estimated to hold 1.2 million tons of ore resources with an average in-situ grade of 2.2% TREO. The run-of-the-mine (ROM) ore is treated by in the Kabezi beneficiation plant, located about 10 km from the project site and about 13 km south of the economic capital Bujumbura, not far from the mine itself. The beneficiation consists of crushing and grinding the Gakara rare-earth ore, followed by removing the gangue by gravity into a rare-earth concentrate, which is further shipped to an off-take intermediary through the ports of Mombasa or Dar es Salaam using road networks linking various East African countries. Unfortunately, despite all of the above, there is a complete lack of information on the substances contained in the concentrate from the Gakara rare earth deposit. And this is precisely the major problem addressed by this study.
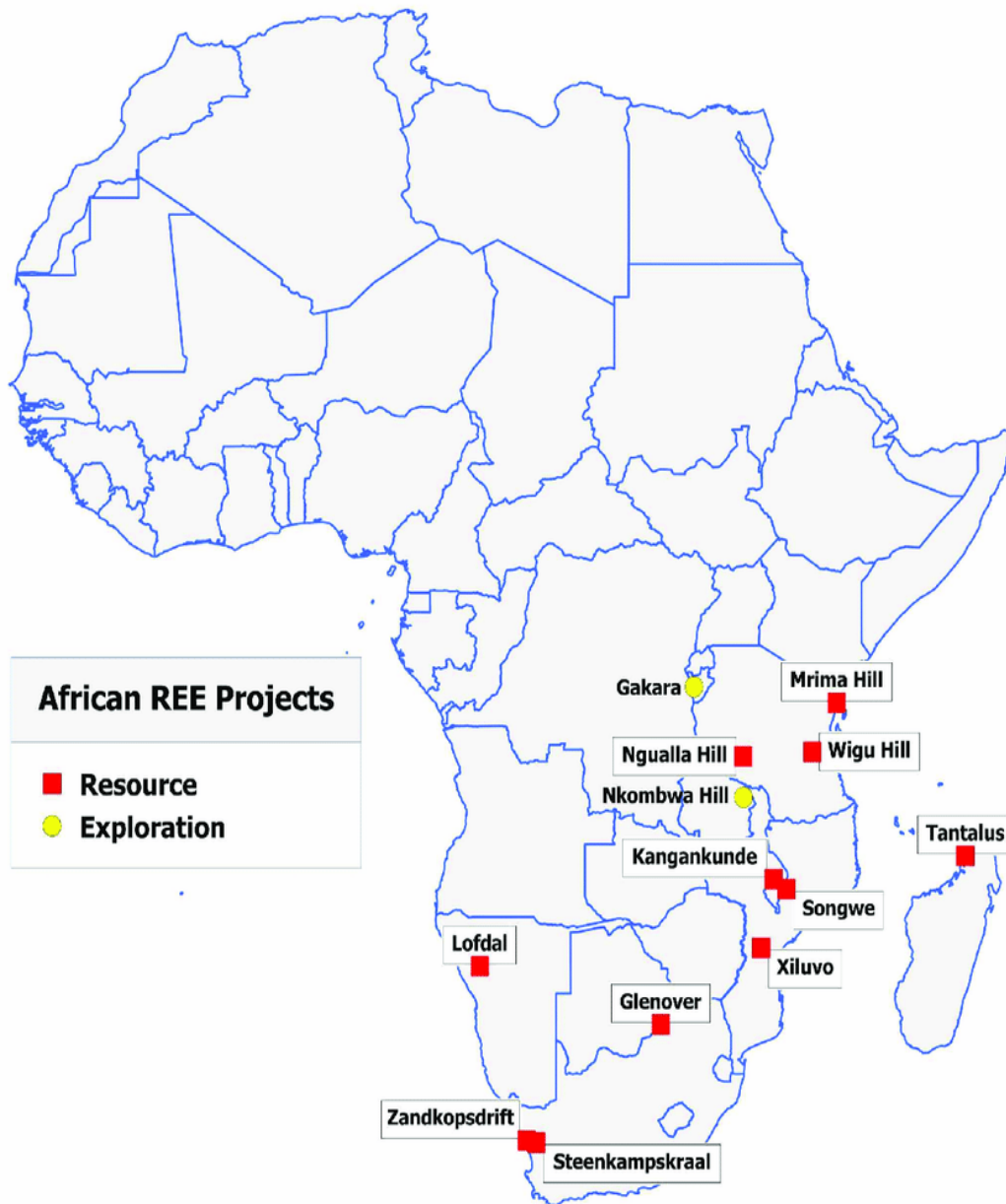
Figure 2: Map showing locations of the African REE projects including the Gakara Rare-Earth Project in Burundi. Reprinted from Rare-Earth Deposits of Africa (Harmer *et al.*, 2016).

It is in view of all the above that the present study was initiated and aimed on quantitative analysis by X-ray fluorescence spectroscopy on two types of samples. Firstly, analyses were carried out on samples of Gakara rare-earth concentrates taken randomly from batches produced and marketed from 2017 to 2020. The purpose was to then consider research into the optimization of an appropriate technological process for the separation, extraction and purification of rare earth metals from said concentrates. Secondly, the same analysis was carried out on samples taken downstream from samples taken from different waste storage sites scattered around the beneficiation plant. The objective of the latter was to determine the quantities of rare-earths possibly remaining in this waste, but also the quantities of thorium, uranium and lead, which are the natural by-products of the monazite deposit. Indeed, the latter, each in its toxic specificity, can prove to be a risk of contamination of the surrounding environment. Especially since the Kabezi beneficiation plant is located only a few dozen meters from Lake Tanganyika, considered the largest freshwater reservoir in Africa and the second largest in the world.
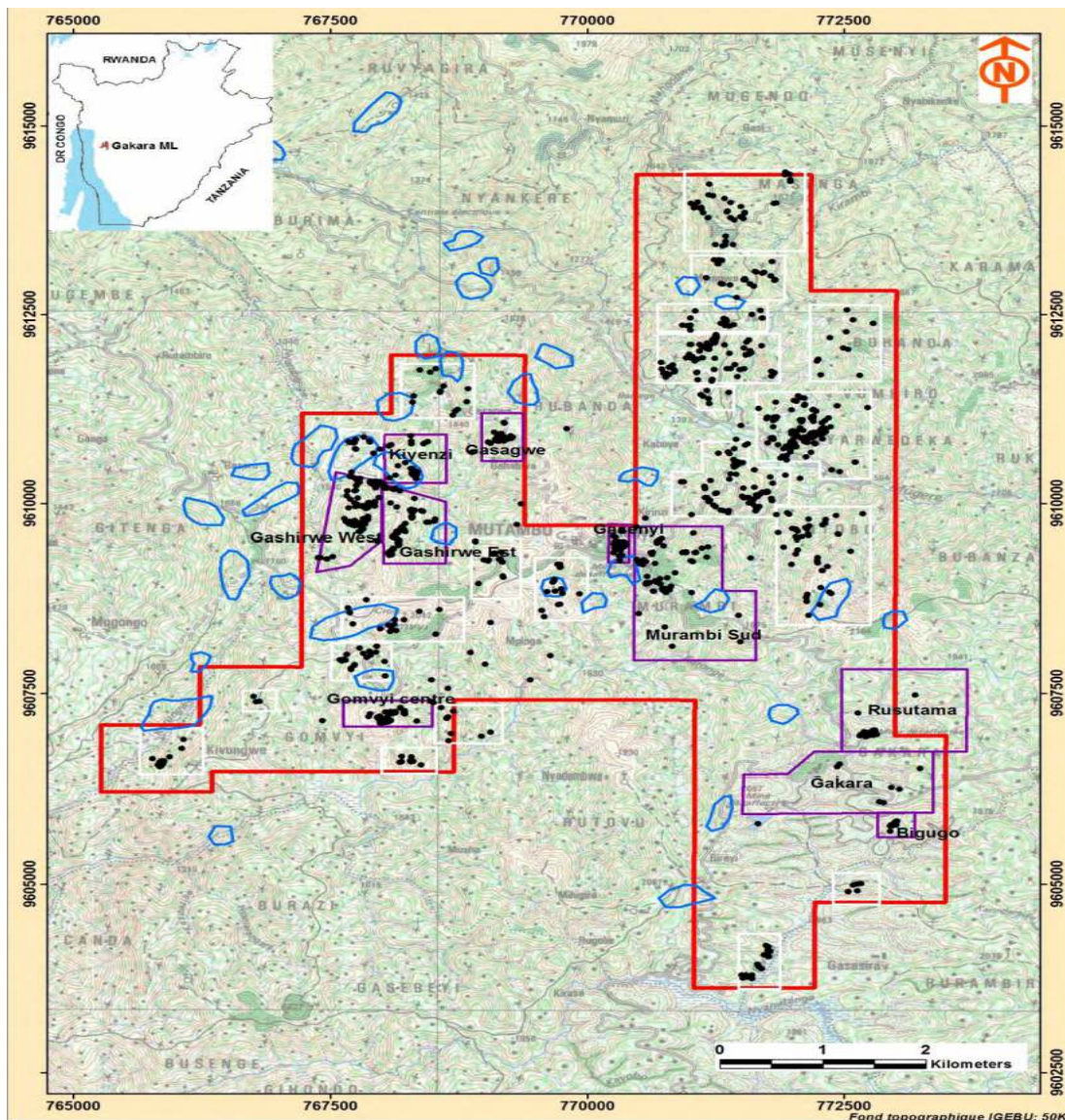
Figure 3: Exploration targets (purple shapes) showing the surrounding identified surface REE mineralization (black dots) of the Gakara Rare-Earth Project. Reprinted from the Technical Report of the Gakara Rare-Earth Project, 2020 (Titley *et al.*, 2020).

2. Materials and Methods

2.1. Sampling and Sample Preparation

All samples analyzed in this study were solid pressed pellets meeting all the conditions required for use with XRF equipment integrated into a factory-configured SQX calibration library thanks to the powerful FP (Fundamental Parameters) software which allows non-empirical calibration to be carried out via a library of pure element standards of metals, glass, oxides and polymers, and thus quantitatively measures any unknown sample with almost empirical precision (Balasubramanian et al., 2016; Rousseau, 2013 Sherman, 1955; Spectroscopy, 2007). One of the FP requirements is that the pellet must be quite flat, very smooth, with a thickness such that no incident X-ray beams will pass through.

The preparation of pressed pellets was carried out at the Burundian Office of Mines and Quarries (OBM). The complete procedure for making pellets, from preparation of the samples, was carried out according to the Rainner Schramm protocol (Schramm, 2012). The first series of solid pellets analyzed in this study were prepared from samples of concentrates, all provided by the Burundian ministry in charge of mines. The Gakara rare-earth concentrate resembles yellowish sandy aggregates (Figure 4a, left). An appropriate amount of a concentrate was carefully ground and reduced to a fine powder. Eight grams of the powder thus obtained was poured into a pellet mold previously well cleaned with ethanol and weighed using an analytical balance. Two grams of organic binder, a Wax, were added to the analyte sample and the mixture in the mold was homogenized for about five minutes by using a mixter (a Mixer/Mill 8000M). The homogenized mixture was then subjected to a pressure of 400 kN for about 2 min in a motorized hydraulic press (a MP250 of Maassen GmbH). Finally, the result are fresh yellowish pellets (Figure 4b, right) of 44 mm

in diameter and less than 10 mm in thickness which are removed from the mold and ready for XRF analysis of its chemical constituents. The sampling involved 8 samples of rare earth concentrate taken in bulk from different batches, produced from December 2017 to 2020. For each sample, three pellets were prepared, i.e. 24 the number of pellets analyzed by WD-XRF. The average obtained for each substance was calculated on the basis of 24 pellets.
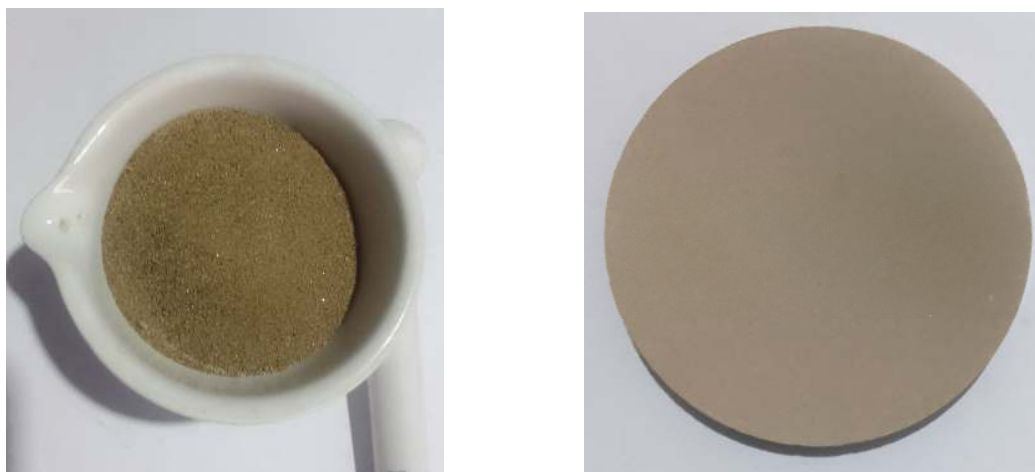
Figure 4: a) The yellowish sandy aggregate of the Gakara rare-earth concentrate (let). **B)** Fresh pellet made from Gakara rare-earth concentrate (right).

The second series of solid pellets analyzed was prepared from samples of solid waste taken in bulk from landfills dumping waste generated by the enrichment process and abandoned at a dozen sites. Samples taken from waste sites were mixed and crushed together to obtain a homogeneous fine powder representative of all the waste dumps. These samples were then mixed together to constitute a single powder, for which a pellet was prepared using the same procedures and protocols as those used for the preparation of rare-earth concentrate pellets.

2.2. Analysis and Instrumental Specifications

In this research study, analysis were performed with a Supermini200, a sequential benchtop wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer branded and manufactured by Rigaku Corporation (Figure 5). It operates under a Windows 10 environment with a built-in software based on the powerful of the Fundamental Parameters (FP) approach to calibration in XRF (Sherman, 1955; Spectroscopy, 2007). Reliable quantitative analysis were achieved thanks to the performance of the following software features: a SQX software with the FP matching library, a SQX scatter FP method, a fused bead correction with a line overlap correction using theoretical intensities (LOCTI), and a Quant Scatter FP method. A Supermini200 is also equipped with the following technical operating built-in devices: a primary Zr-beam filter, a Pd-anode X-ray tube with a power of 200 W produced by a 50 kV and 4 mA generator. It also uses standard crystals of lithium fluoride LiF(200) and pentaerythritol PET(002). As for the detectors, the Supermini200 is equipped with a set of detectors based on the Pulsed Height Analyzer (PHA) with a scintillation counter (SC) for heavy metals, and a gas-flow proportional counter (F-PC) for light elements. All this ensures high sensitivity and high-speed counting.


Figure 5: The sequential benchtop wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer, a Supermini200 branded and manufactured by Rigaku Corporation.

3. Results and Discussion

3.1. Qualitative Results of XRF Analysis

In XRF analysis, each element has its own signature, represented by a peak in the spectrum of the sample. Therefore, the set of peaks in an XRF spectrum forms the characteristic signature of the sample. Thus, the WD-XRF spectrum in Figure 6 is the unique and specific signature of the Gakara rare-earth deposit. At first glance, such a spectrum indicates that the sample contains several substances, including rare-earths and other associated substances. The spectrum of the Gakara REEs has three K-lines and about seven L-lines which could be used. However, the sensitivity of the analyte lines differs a lot. From the K-line series, the $K_{\alpha1\alpha1}$ line and for the L-lines, the $L_{\alpha1\alpha1}$ and $L_{\beta1\beta1}$ show the highest sensitivity, as predicted for the WD-XRF analysis.
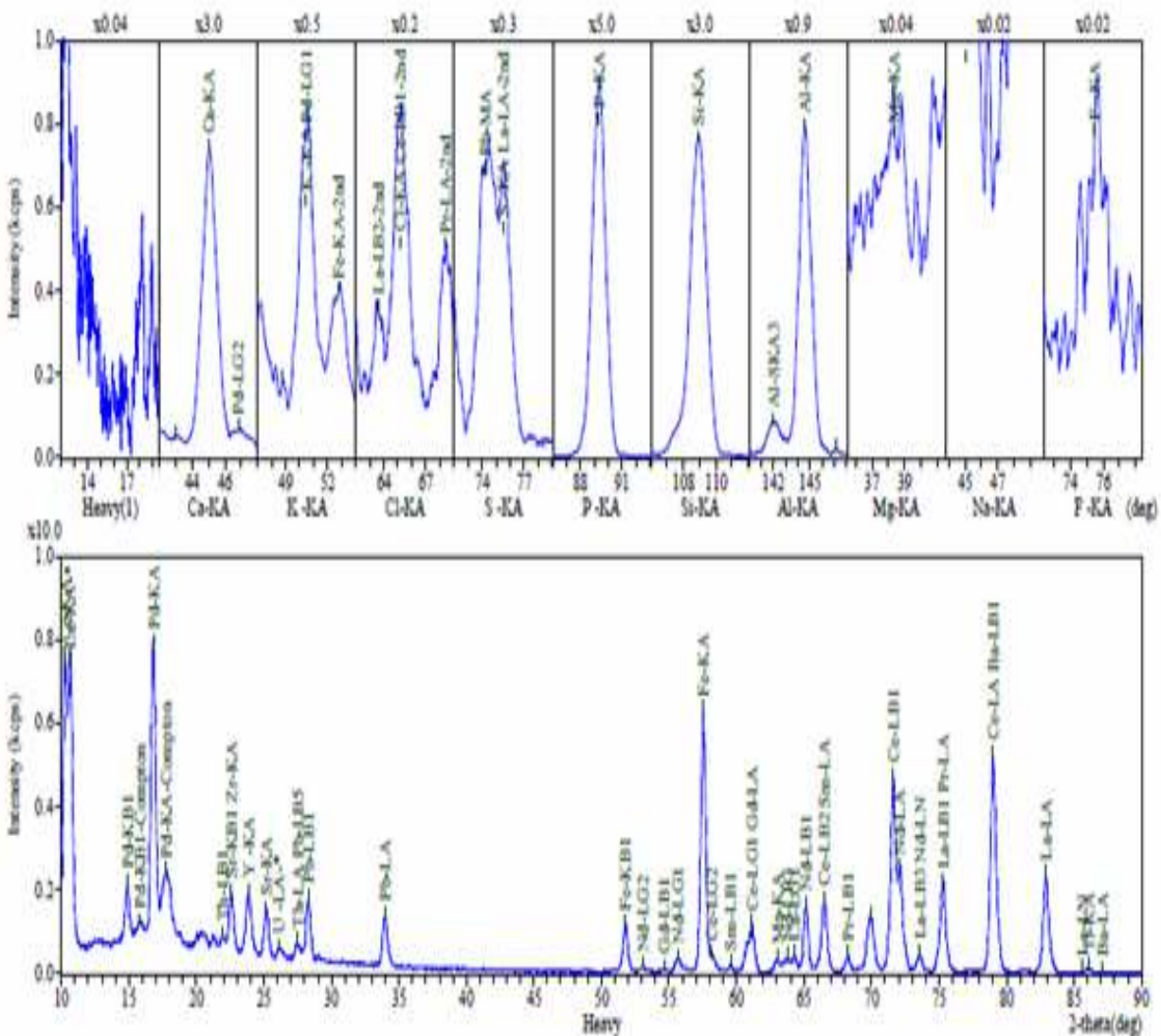
Figure 6: Qualitative analysis result of a WD-XRF spectrum typical to the Gakara rare-earth concentrate.

The WD-XRF spectrum also indicates a Kα peak for Yttrium, Lα peaks for La and Nd, and L$_\beta$ peaks for cerium and praseodymium. These are all high energy XRF absorption peaks. The blurry appearance of the XRF spectrum of Figure 5 is due to matrix effects, which cause pics overlap. Fortunately, this does not affect the quantitative results because the XRF machine counts and assigns characteristic photons to the element that really produces them, not to the other element which emits at the same energy and eventually overlaps with it.

3.2. Quantitative XRF Analysis Results of Gakara Rare-Earth Concentrate

Quantitative results are recorded in Tables 1 and 2 below for the analysis of the concentrate, and in Table 3 for the analysis of solid wastes. Two illustrative graphs are also presented for better interpretation and discussion of the results.

Table 1. Rare-earth elements and associated elements substances contained in the Gakara rare-earth concentrate. Total Rare-Earth Elements (74.70% TREE). Average taken from 24 pellets (3 pellets for each of 8 samples of rare earth concentrate).

Elements	Y	La	Ce	Pr	Nd	Sm	Gd
Concentration (% w/w)	0.159±0.014	20.525±0.778	37.750±0.602	2.806±0.255	12.137±0.410	1.012±0.175	0.471±0.092
Elements	Mg	Al	Si	P	S	K	Ca
Concentration (% w/w)	0.280±0.047	1.208±0,168	5.765±0.860	5.850±0.200	0.600±0.186	0.634±0.180	1.022±0.077
Elements	Mn	Fe	Sr	Ba	Pb	Th	U
Concentration (% w/w)	0.236±0.040	7.069±0.516	0.167±0.020	2.084±0.536	0.814±0.128	0.101±0.009	0.082±0.006

Table 2. Rare-earth oxides and associated oxide substances contained in the Gakara rare-earth concentrate. Total rare-earth oxides (65.78% TREO). Average taken from 24 pellets (3 pellets for each of 8 samples of rare earth concentrate).

Oxides	Y_2O_3	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Gd_2O_3
Concentration (% w/w)	0.149±0.004	17.986±0.653	33.750±0.652	2.629±0.202	10.003±0.269	0.906±0.090	0.407±0.040
Oxides	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO
Concentration (% w/w)	0.422±0.126	1.800±0.291	9.705±1.465	9.136±0.699	1.155±0.392	0.582±0.178	1.076±0.084
Oxides	MnO	Fe_2O_3	SrO	BaO	PbO	ThO_2	U_3O_8
Concentration (% w/w)	0.200±0.024	7.342±0.552	0.139±0.012	1.602±0.509	0.622±0.110	0.079±0.005	0.072±0.009

The results of analysis of the rare-earth concentrate produced by the Gakara rare-earth deposit beneficiation plant contains seven rare-earth metals (Table 1) or rare-earth oxides (Table 2), in varied proportions. The stoichiometric distribution of each rare-earth in the concentrate is shown in Figure 6. The composition in oxides contained in the Gakara rare-earth concentrate in terms of its three major components is also highlighted in Figure 6. The seven rare-earths together have a total rare-earth oxides (TREO) content of 65.78 ± 0.29%, and a total rare-earth elements (TREE) content of 74.84 ± 0.33% (Figure 7). The other associated substances of interest present in the concentrate are Th (0.101%; 0.079%). Even if there is no known market at the present, Th has technological applications mainly linked to its refractory nature (it melts at 2000 °C) in addition to being the ecological fuel of the future in nuclear power plants for the production of electrical energy. The presence of phosphates is an indicator of a monazite deposit. These quantities (5.850%; 9.136%) are enough for being considered as basic raw material for the formulation of chemical fertilizers in a small to medium plant. The presence of Pb (0.814%; 0.622%), which is a radioactive decomposition element of thorium, is an indication of a monazite deposit. Although part of heavy elements that can be harmful to the environment (lead poisoning is as harmful as arsenic or mercury poisoning), lead is mainly used in automobile batteries. Other substances other than those described above are also important and are often indicative of a specific mineralization. The presence of important quantities of P_2O_5 (9.136%) is an indication of a monazite-Ce ($CePO_4$) based mineralization ore. The concentrate also contains important oxides as SiO_2 (9.705%) and in Fe_2O_3 (7.342%), but also minor quantities of Al_2O_3 (1.797%), MgO (0.422%), K_2O (0.582), CaO (1.076%), SrO (0.139%) and BaO (1.602%). All these oxides are generally carbonites associated to bastnaesite mineralization. This confirms the thesis that the Gakara rare-earths deposit is mineralized in both monazite and bastnaesite.
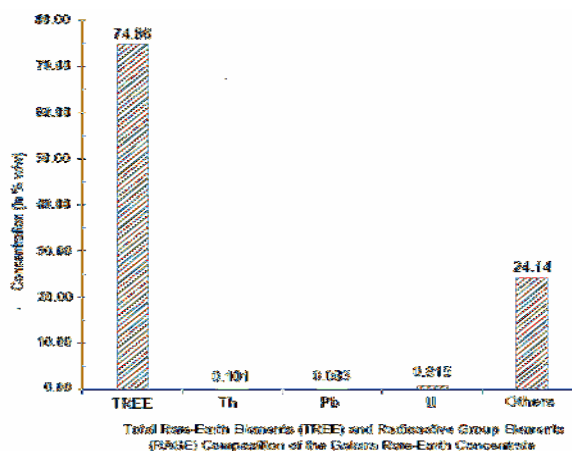
Figure 7: Total rare-earth elements (TREE: 74.86 ± 0.33%) of the Gakara rare-earth concentrate. Radioactive group elements include Th (0.101±0.009%), Pb (0.814±0.128%) and U (0.082±0.006%). Other associated substances totalize 24.14%.

The great particularity of the Gakara rare-earth deposit is such that, of the seven rare-earths present in its concentrate, four are part of the seven rare-earths which have been qualified as critical by the US Government (Haxel *et al.*, 2018) due to the supply chain threats which weigh on them, while they are involved in high military strategic technologies. These are neodymium, samarium, praseodymium and yttrium. The United States dependence on imports from China comes at a time where REEs have become increasingly important in defense applications.

It is also important not to lose sight of the fact that the Gakara rare-earth concentrate contains quantities, although minimal, of thorium and uranium, which must be eliminated from the mixture and stored safely. The techniques for separating thorium and uranium are well known and are the same ones used for the separation and purification of rare-earths (Talan *et al.*, 2020; Zhu *et al.*, 2015). Unfortunately, all these techniques of liquid-solid extraction, for being based on the property that all mineral elements have to precipitate at specific pH, consume a lot of acids and bases, which can turn out to be very voluminous if we look at the number of minerals contained in the concentrate, including the seven rare-earths, the three elements of the thorium group (Th, U and Pb), as well as the dozen other associated minerals (SiO_2, Fe_2O_3, PO_4, etc.)

3.3. Quantitative XRF Analysis Results of Solid Waste Generated by the Beneficiation Plant of the Gakara Rare-Earth Deposit

Table 3 gives the result of XRF analysis of these solid waste, in which one can see significant quantities of REEs, but also two elements associated with the radioactive group of thorium (Th, Pb and U). The analysis results indicate that in the waste dumps, there are still significant quantities of rare-earths, with a content of 10.10% TREE as can be seen in Table 3 and Figure 7. This content is significant so as not to be neglected. Indeed, these are five metals out of the seven initially present in the concentrate. In fact, one can see that samarium and gadolinium are not present in any of the waste. Among the five REEs detected in solid waste, the most abundant are Ce (5.38%), followed by La (2.80%) and Nd (1.41%). The other associated substances present in solid waste are elements associated with the radioactive group elements (RAGE) including Pb (0.24%) and Th (0.13%). Although uranium is absent from the list, this does not mean that it is not present in the waste dumps. Specific analysis with techniques capable of detecting even traces, for example ICP, should be carried out to ensure that there is no uranium in the environment.

Table 3. Rare-earth elements, thorium group elements and associated substances contained in the Gakara rare-earth beneficiation waste dumps. Low detection limit (LDL): approximately 10 μg/g

Elements	Y	La	Ce	Pr	Nd	Sm	Gd
Concentration (% w/w)	0.108	2.800	5.380	0.402	1.410	*	*
Elements	**Pb**	**Th**	**U**	**Mg**	**Al**	**Si**	**P**
Concentration (% w/w)	0.237	0.127	*	0.781	13.400	47.500	1.380
Elements	**S**	**K**	**Ca**	**Mn**	**Fe**	**Sr**	**Cl**
Concentration (% w/w)	0.064	8.000	0.361	0.228	16.700	0.092	0.051

*Not detected
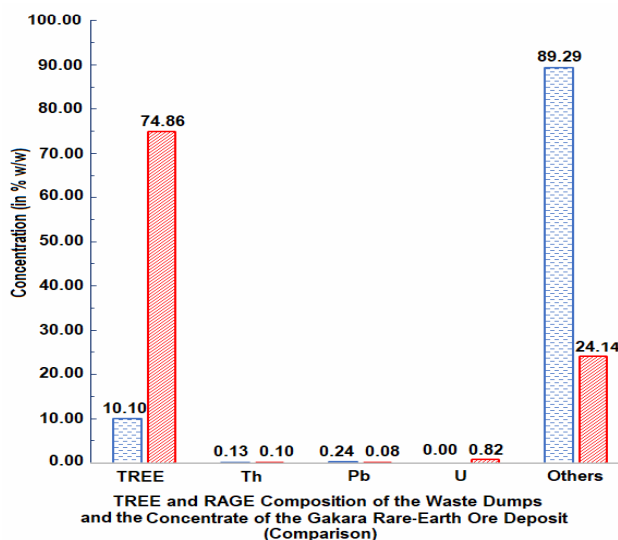
Figure 8: Comparison of the elementalcomposition of products from the Kabezi beneficiation plant: waste dumps (blue horizontal dashes, left) and rare-earth concentrate (red oblique dashes, right)

Although the beneficiation by gravity method is generally best suited for rare-earth mines with mineralization such as that of the Gakara mine, a review of all enrichment protocols and processes is necessary to reduce the presence of certain elements in waste dumps to the strict minimum. Indeed, the 10% TREE content, obtained from samples collected in bulk on all the dumps, is far higher than the on-site (in-situ) contents of most rare-earth deposits in operation, and even often praised by owner countries. One can cite the Wicheeda mine in British Columbia, Canada, which has an in-situ grade of 2.95% TREO (Trofanenko, 2014); the famous Mountain Pass bastnaesite mine in California, United States, with a maximum of 10% TREO (Castor, 2008); and finally, the Ashram mine in Quebec, Canada, with a maximum in-situ grade of 1.90% TREO (Costis *et al.*, 2021). Ultimately, the enormous quantities of residues generated by the Kabezi enrichment plant could be considered as another source of rare-earth feedstock that should not be neglected. Moreover, to the extent that these dumps are scattered over unsecured sites, they constitute a danger for the environment: The Lake Tanganyika, a rich heritage shared by five countries in Africa, is located a few meters from the beneficiation plant and some of these waste dumps may have started to drip their heavy water directly into the lake.

Finally, it is important to note that all oxides detected by XRF in waste are also those used in cement formulation. A preliminary simulated calculation was carried out on the three quality parameters used for cement and from the data obtained in this study, namely the lime saturation factor (LSF), the silica content (SR) and the ratio of alumina (AR). We noted that, apart from the LSF which is too low, and therefore indicative of a deficit in calcium oxides, the other parameters (SR and AR) appear to be within the limits of known standards for cements. We therefore conclude that the waste from the Kabezi beneficiation plant could be considered as a potential source of basic raw material for the formulation of a quality cement that could be formulated with rare earth waste and other waste rich in calcium oxides to be identified.

4. Conclusion

The objective of this study was to assess the products and by-products contained in the rare earth concentrate from the Gakara ore deposit in Burundi using wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF). The same study was carried out on the waste discharges generated by the concentration plant. The Gakara rare earth deposit is a high-grade LREE deposit consisting of a mixture of bastnaesite and monazite. The key findings of this research work reveal that the Gakara rare-earth deposit is rich in seven rare earths involved in high technologies, particularly those requiring the use of devices or equipment requiring super magnets. These are Nd (12.14% in element); 10.00% in oxide), followed by Pr (2.80%; 2.63%), Sm (1.00%; 0.90%) and Y (0.16%; 0.15%). Other important rare-earths found include Ce (37.75%; 33.75%), La (20.5%; 18.0%) and Gd (0.47%; 0.35%). These seven rare-earths together have a total rare-earth oxide (TREO) content of 65.78 ± 0.29% and a total rare-earth element (TREE) content of 74.84 ± 0.33%.

The scope for future research should therefore focus on the optimization of a rare-earth separation and purification process specific to the Gakara rare-earth concentrate in terms of quality/cost ratio, while considering environmental concerns. As Burundi does not yet have a mining industry despite its rich and varied mineral resources, the construction of a rare-earth concentrates processing plant using such a technological process could then lay the foundations for the development of a mining industry at a large scale; and not only for these highly strategic metals, but also for other ores known for their difficulty in processing, such as Coltan and others. Specifically, it is proposed to consider the latest developments in preparative displacement chromatography, in particular the multi-dimensional ligand-assisted chromatography and the simulated moving bed (SMB) systems, developed and patented by Professor Linda Wang of Purdue University.

Concerning waste dumps, future research perspectives could focus on the possibility of valorizing industrial waste, including those from the Kabezi rare earth beneficiation plant, through the identification of basic raw materials for the formulation of quality cement for the manufacture of geomaterials of public interest, such as concrete, ceramic tiles, etc.

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